Production Of Propionic Acid From Syngas

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29. **EXECUTIVE SUMMARY**
    1. Abstract

With an estimated world production of capacity of 377,000 metric tons in 2006, Propionic Acid is an important organic acid that does not receive much publicity. Propionic Acid – which occurs naturally in apples, strawberries, grains, cheese, and human sweat – is mainly used as a mold inhibitor for various animal feed and baked goods as well as a preservative in cheeses. It is also a significant precursor in many industrial processes such as pharmaceuticals, plastics, plasticizers, textile and rubber auxiliaries, dye intermediates, as well as flavorings and cosmetics. Our group has designed a chemical plant for the production of Propionic Acid with a projected output of 33,000 tons per year. The initial feedstock will comprise of Sygnas (a mixture of CO and H­2) and Ethylene, which will react in a process known as carbonylation in the presence of a catalyst to produce Propionaldehyde. The Propionaldehyde will then be oxidized to produce Propionic Acid. The market demand for Propionic Acid is expected to grow at around 2.3% per year regardless of the state of the economy since food production and preservation is highly dependent upon it. With a steadily increasing market price and demand for Propionic Acid along with its marketability in other industrial processes combined with its high price relative to our cheaper reactants and catalysts should make the proposed plant a very economically feasible one.

1. **DISCUSSION** 
   1. **Process Overview**

The process was chosen because of a wide range of applicable standards in which the final product can be used. While the food industry will be a main target of team echo, other avenues will also be explored, see Appendix XIII.

* + 1. Production of Propionaldehyde

Ethylene will be obtained at 450 psi pressure and 158 ° F temperature. Syngas will be obtained at the prescribed temperature and pressure of 290 psi and 212 ° F. Ethylene will be heated to 212 ° F which is the reaction temperature. Both ethylene and syngas will be fed into the reactor at the reaction specifications in order to produce propionate. Propionate is a precursor to Propionic acid, and is the aldehyde for of Propionic acid. The conversion of the reactants to Propionate is not one hundred percent and thus there will be unreated reactants in the product stream. The majority of the unreacted reactants will be flashed out of the product stream to temp 70° F and pressure 14.7 psi. The recycle stream will be recompressed and cooled back to the reaction conditions before being recycled back into the reactor. The purified product stream will be sent on to the second reaction process which will oxidize the propionate to its carboxylic acid form of Propionic acid.

A heat exchange reactor will be used to carry out the reaction and will be purchased from Chart Energy & Chemicals, Inc. It will be made of stainless steel, which is more expensive that carbon steel, but the corrosive properties of Propionaldehyde are unable to be supported by carbon steel and would create an unsafe situation. The reaction will be catalyzed using a rhodium catalyst which will be immobilized in the reactor. Because of this, separation of the catalyst is not a problem and because rhodium has a very long shelf life it will not have to be bought often.

* + 1. Oxidation of Propionaldehyde

The propionate product from the first reaction is heated to the proper reaction conditions temp 122° F and pressure 14.7 psi. Oxygen is used to oxidize the aldehyde into its carboxylic acid form. Oxygen is brought in at ambient conditions and heated to the proper temperature using a feed-effluent heat exchanger. Propionic acid is produced in this reaction, with unreacted reactants and catalyst also flows from the reactor. A cobalt iodide slurry is used to catalyze the reaction and the water component of this mixture is miscible with the Propionic acid final product. The cobalt halide is precipitated and filtrated out of the final product and flushed from the system. The water, however, is still in the final product and must be separated in order to meet the industry specification of 99.5% purity. In order to meet this specification the product-water mixture was decanted, then sent into a distillation column to be further concentrated. The industry standard was met and exceeded with a purity of 99.8%.

1. **CONCLUSIONS AND RECOMMENDATIONS**
2. **Appendices**
3. Design Basis
   * 1. Commercial Production

Propionic Acid – which occurs naturally in apples, strawberries, grains, cheese, and human sweat – is mainly used as a mold inhibitor for various animal feed and baked goods as well as a preservative in cheeses. It is also a significant precursor in many industrial processes such as pharmaceuticals, plastics, plasticizers, textile and rubber auxiliaries, dye intermediates, as well as flavorings and cosmetics.

* + 1. Environmental Review

As responsible engineers it becomes necessary to become concerned not only with how much money a process will be able to make but also with safety measures as well. Safety for the workers in the plant and safety for the environment, with the latter being the focal point of this section. Engineers have an ethical responsibility to ensure that in their efforts to improve the quality of life for mankind that a paradox is not created.

Industrially, the majority of Propionic Acid is used as a bactericide and fungicide to protect hay and grains that are being stored as well as an ingredient for pesticides. This is possible because it has been EPA certified to have low toxicity to fish, invertebrates, birds and mammals. Propionic acid is used primarily indoors and use outdoors in small amounts, when used outdoors, Propionic acid was metabolized by organisms into harmless components and has thus been deemed not harmful to the environment. Propionic acid is non-mutagenic and has overall been observed to not be harmful. Contact with concentrated solutions of Propionic acid however, may cause damage to eye and bodily membranes as the solution is corrosive. Protective clothing should be used when handling the compound in its purer forms.

Propionaldehyde is the intermediate product produced in the two step reaction and while it is only available in small amounts in the final product it is still necessary to know as much about this as possible. Propionaldehyde, according to the EPA, is not a carcinogen, nor does it have any reproductive effects on humans. Chronic effects: adverse effects on the body with symptoms that develop slowly due to prolonged exposure to something harmful and do not subside once the exposure is no more, are not associated with exposure to Propionaldehyde. Acute effects on the other hand, adverse effects that subside once exposure is terminated, results have proved to be inconclusive in the human though animals have shown moderate to acute toxicity to the substance.

Rhodium is a very rare platinum group element. It is combustible in dust when in the powder form. Rhodium is quite toxic if inhaled, though this will not be a problem as the Rhodium based catalyst will be used on graphite supports and immobilized in a packed bed. It is good that very little handling of Rhodium will be necessary as it is also a skin irritant. There are very strict regulations as how to dispose of Rhodium. As Rhodium is a very rare element is it unknown whether or not it is harmful to the environment, and is not currently classified as harmful to the environment.

A Cobalt catalyst is used in the oxidation of Propionaldehyde to Propionic acid. Cobalt Iodide generally has a low toxicity; however, there are acute and chronic effects when exposed to larger amounts of Cobalt iodide. Acute effects include: shortness of breath, systemic effects, skin irritation, eye irritation, and cornea damage. Chronic effects include: respiratory sensitivity, nodular fibrosis, thyroid disease, pimples, boils, black and blue spots, hives, and blisters. The probability of these effects occurring is minimal as contact with the chemical is extremely limited and controlled. Operation of Cobalt Iodide will not be performed without safety clothing and a breathing apparatus.

* + 1. Specifications to Meet Industry Standards

The industry standard for Propionic acid is currently to have a 99.5 mol% purity. In order to achieve this goal the product will be separated many times throughout the process before the reaching a distillation column in which the final product will be obtained. The column was designed around the basis of having a 99.5% purity of Propionic acid. This basis was exceeded as the Propionic acid leaving the process has a 99.8% purity.

* + 1. Clear Statement of Feedstock

The feedstock to be used in this process is synthesis gas made by team Foxtrot and Ethylene obtained from Lyondell Basell. The synthesis gas or syngas will be created from coal obtained from Illinois coal basin number 6 in southern Il. Because coal is being used as a source for syngas, the coal will have to be heavily treated in order to have it meet the specifications of the process. Desulfurization and CO2 sequestration are only two of the processes that take place in the purification of syngas in order to obtain a 1:1 mole ratio of CO to H2. The conditions at which the syngas will be delivered will be the necessary conditions for the production of Propionaldehyde.

The other feedstock for the synthesis of propionate is ethylene. It will be obtained by pipeline an industrial standard purity. It will be obtained at 420 psig and 70 °F which is near the conditions of the reaction.

Oxygen will be fed into the second reaction which is the oxidation of Propionate to Propionic acid. Oxygen will be obtained from the air around and thus is assumed to be at ambient conditions.

* + 1. Engineering Design Standards

1. Block Flow Diagram

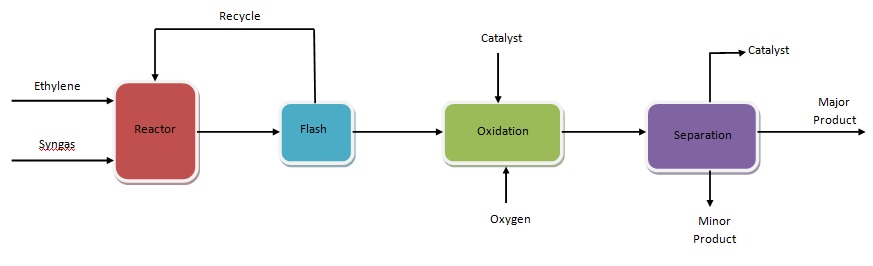


Figure II.1: Block Flow diagram

In the above figure, a generic version of the process is shown in order to glean a generic sense of what is happening in the process before going looking at the more detailed flowsheet and process flow diagram.

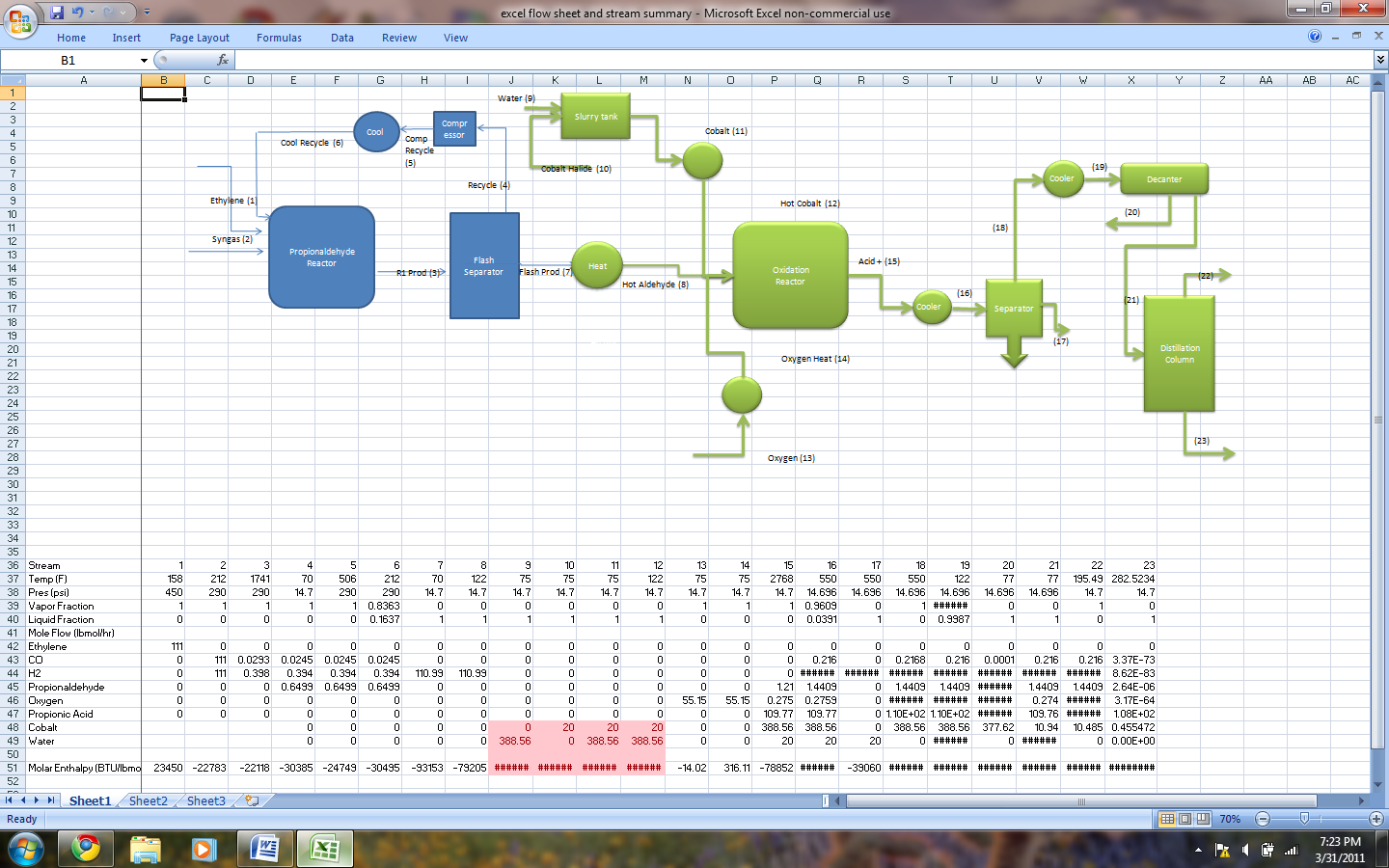


Figure II.2: Overall Flowsheet of system

Figure II.3 is pictorially shows the process of how to produce Propionic acid. The process flowsheet will be broken down into components with stream summary in order to make it easier to read.

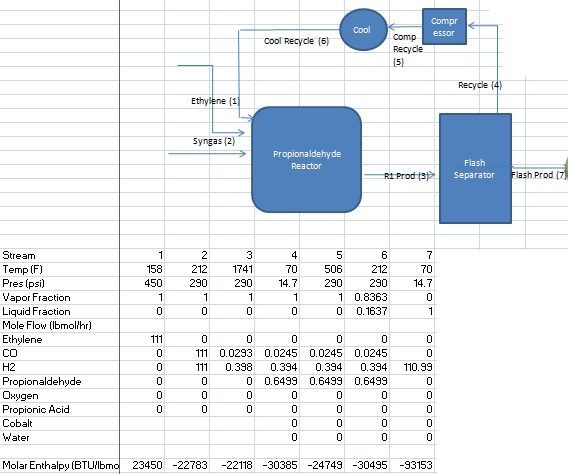


Figure II.3: Production of Propionaldehyde

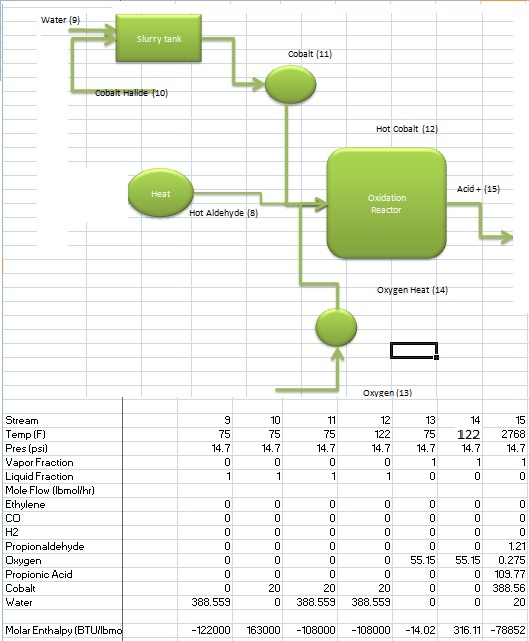


Figure II.4: Production of Propionic Acid

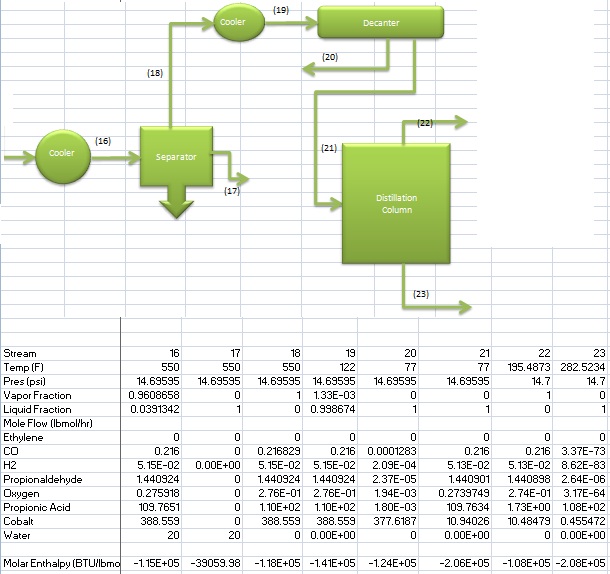


Figure II.5: Purification of Propionic Acid

1. Process Flow Diagram
2. Material and Energy Balances
3. Calculations
4. Annotated Equipment list

|  |  |
| --- | --- |
| Equipment Piece | Description |
| Reactor 1 | Produces Propionaldehyde from Syngas and Ethylene |
| Reactor 2 | Oxidizes Propionaldehyde to Propionic Acid |
| Compressor |  |
| Cooler (HX) |  |
| Heat (HX) | Heats Oxygen entering the system in order to carry out the oxidation reaction |
| Heater (HX) | Heats the propionaldehye stream leaving the flash separator, before it enters the oxidation reactor |
| HX (HX) | Cools oxidized final product before it enters the distillation column |
| Flash | Separates Propionaldehyde from unreacted reactants before the Propionaldehyde can be oxidized |
|  |  |
| Cocat Separation |  |
| Cooler |  |
| decanter |  |
| Dist- bottoms split |  |
| Dist-cond |  |
| Dist-cond acc- horizontal drum |  |
| Dist- reboiler |  |
| Dist- reflux pump |  |
| Dist- tower |  |
| Heat |  |
| Separator |  |
|  |  |
|  |  |

Chart VI.1

|  |  |  |  |
| --- | --- | --- | --- |
| Equipment Piece | E Cost | D Cost | Sizing |
| Reactor 1 |  |  | Liquid volume- 250 gal |
| Reactor 2 |  |  | Liquid volume- 250 gal |
| Compressor | 1140500 | 1236300 | Actual gas flow inlet – 4.18959 CFM  Driver Power- 1.4393386 HP  Specific Heat Ratio- 1.214862  Turbine gauge pressure – 300 Psig  Lube oil system- yes |
| Cooler (HX) | 15300 | 136600 | Heat Transfer area- 0.0688888 SF  Tube design gauge pressure- 325.3795 psig  Tube design temperature- 556.445 deg F  Tube operating temp- 506.445 deg F  Shell design gauge pressure- 212.021 psig  Shell design temp- 250 deg F  Shell operating temp- 95 deg F  Tube length extended- 20 feet  Tube wall thickness- 0.125 in  Tube seal type- seal welded tube joints  Tube pitch- 1.25 in  Tube pitch symbol- Triangular  Expansion joint- NO  Cladding location- Shell  # Tube passes- 2  # Shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vandor grade- High  Regulation Type- None |
| Heat (HX) | 8000 | 44900 | Heat transfer area- 3.2668 SF  Tube design gauge pressure- 110.304 psig  Tube design temp- 377.8 deg F  Tube operating temp- 327.8  Tube outside diameter- 1in  Shell design gauge pressure- 68.6373 psig  Shell design temperature- 250 deg F  Shell Operating temp- 122 deg F  Tube length extended- 20 ft  Tube wall thickness- 0.125 ft  Tube seal type- seal welded tube joints  Tube pitch- 1.25 in  Tube pitch symbol- triangular  Expansion joint- No  Cladding location- shell  # tube passes- 2  # shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vendor grade- high  Regulation type- none |
| Heater (HX) | 9600 | 57200 | Heat transfer area- 62.9533 SF  Tube design gauge pressure- 110.304 psig  Tube design temp- 377.8 deg F  Tube operating temp- 327.8  Tube outside diameter- 1in  Shell design gauge pressure- 68.6373 psig  Shell design temperature- 250 deg F  Shell Operating temp- 122 deg F  Tube length extended- 20 ft  Tube wall thickness- 0.125 ft  Tube seal type- seal welded tube joints  Tube pitch- 1.25 in  Tube pitch symbol- triangular  Expansion joint- No  Cladding location- shell  # tube passes- 2  # shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vendor grade- high  Regulation type- none |
| HX (HX) |  |  | Heat transfer area- 234.45499 SF  Tube design gauge pressure- 35.304 psig  Tube design temp- 2817 deg F  Tube operating temp- 2767 deg F  Tube outside diameter- 1in  Shell design gauge pressure- 60.304 psig  Shell design temperature- 250 deg F  Shell Operating temp- 95 deg F  Tube length extended- 20 ft  Tube wall thickness- 0.125 ft  Tube seal type- seal welded tube joints  Tube pitch- 1.25 in  Tube pitch symbol- triangular  Expansion joint- No  Cladding location- shell  # tube passes- 2  # shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vendor grade- high  Regulation type- none |
| Flash |  |  | Application: Standard continuous process vessel  Liquid Volume- 863.707858 gallons  Vessel diameter- 3.5 feet  Vessel tangent to tangent height- 12 feet  Design gauge pressure- 325.379475  Fluid volume- 20%  Design Temp- 1790.77608 deg F  Operating Temp- 1740.77608 deg F  Manhole diameter- 18 in  Allowance for internals- 0%  ASME design basis- D1NF  Start Stop cycles \* 1000- 5  Pressure cycles \* 100- 0  Pressure amplitude- 0%  # of hydrostatic tests- 20  Temperature cycles \* 1000- 0  Temperature amplitude- 0% |
| Dist- bottoms split |  |  |  |
| Dist-cond |  |  | Tube design gauge pressure- 150 psig  Tube outside diameter-1 in  Shell design gauge pressure- 150 psig  Tube seal type- seal welded tube joints  Tube pitch symbol- triangular  Expansion joint- No  Cladding location- shell  # tube passes- 1  # shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vendor grade- high  Regulation type- none |
| Dist-cond acc- horizontal drum | 15300 | 136600 | Application- standard continuous process vessel  Liquid Volume- 475.920655 gal  Vessel Diameter- 3 feet  Vessel Tangent to tangent length- 15 feet  Vacuum design gauge pressure- -14.696 psig  Design temp- 32 deg F  Operating temp- -386.630402 deg F  Manhole diameter- 18 in  # manholes- 1 |
| Dist- reboiler | 12500 | 59300 | Heat Transfer area- 95.5056  Tube design gauge pressure- 110.304 psig Tube design temperature- 377.8 deg F  Tube design operating temperature- 327.8 deg F  Tube outside diameter- 1 in  Shell design gauge pressure- 68.6373 psig  Shell design temp- 333.1601 deg F  Shell operating temp- 283.1601 deg F  Tube length extended- 20 feet  Tube wall thickness- 0.125 in  Tube pitch- 1.25 in  Tube pitch symbol- triangular  Cladding location- shell  # tube passes- 2  Duty- 0.48711 MMBTU/hr  Vaporization- 90%  Specific gravity tower bottoms- 0.5  Mol. Weight bottoms- 100  Heat of vaporization- 150 btu/lb  TEMA type- BKU |
| Dist- reflux pump | 4200 | 25300 | Casing material- Carbon steel  Liquid flow rate- 0.302487  Fluid head – 225 feet  Fluid specific gravity- 1.039488  Driver type- motor  Seal type- single mechanical seal  Design gauge pressure- 15 psig  Design temperature- 32 deg F  Fluid viscosity- 0.5 Cpoise  Pump efficiency- 70%  Steam gauge pressure 400 psig  Primary seal pipe plan- none  Secondary seal pipe plan- none  Cooling water pipe plan- none  Pipe plan pipe type- welded pipe/fittings |
| Dist- tower | 308300 | 489700 | Tray type- sieve  Application- distil  Vessel diameter- 1.5 feet  Vessel tangent to tangent height- 108 feet  Design gauge pressure- 15 psig  Design temperature- 333.160142 deg F  Operating temperature- 283.160142 deg F  Tray material- A285C  # Trays- 48  Tray spacing- 24 in  Cladding materials- none  Fluid volume- 20%  Jacket type- full  Jacket Material- Carbon Steel  Molecular weight product- 73.999443  Tray thickness- 0.1875 in  ASME design basis- D1NF (Division 1, no fatigue)  Start Stop cycles \* 1000- 1  Pressure cycles \* 100- 0  Pressure amplitude- 0%  # of hydrostatic tests- 20  Temperature cycles \* 1000- 0  Temperature amplitude- 0% |
|  |  |  |  |
| Cocat Separation |  |  |  |
| Cooler | 15100 | 74200 | Heat Transfer area- 330.859382 SF  Tube design gauge pressure- 35.304 psig  Tube design temperature- 600 deg F  Tube operating temp- 550 deg F  Shell design gauge pressure- 60.304 psig  Shell design temp- 250 deg F  Shell operating temp- 95 deg F  Tube length extended- 20 feet  Tube wall thickness- 0.125 in  Tube seal type- seal welded tube joints  Tube pitch- 1.25 in  Tube pitch symbol- Triangular  Expansion joint- NO  Cladding location- Shell  # Tube passes- 2  # Shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vandor grade- High  Regulation Type- None |
| Decanter | 15800 | 102400 | Liquid Volume- 634.560878 gal  Vessel diameter- 3  Vessel tangent to tangent diameter- 12 feet  Design gauge parameter- 15 psig  Vacuum design gauge parameter- -14.696  Design temp- 250 deg F  Operating temp- 122 deg F  Fluid volume- 20 %  Manhole diameter- 18 in  Allowance for intervals- 0  ASME design basis- D1NF (Division 1, no fatigue)  Start Stop cycles \* 1000- 1  Pressure cycles \* 100- 0  Pressure amplitude- 0%  # of hydrostatic tests- 20  Temperature cycles \* 1000- 0  Temperature amplitude- 0% |
| Dist- bottoms split |  |  |  |
| Dist-cond |  |  | Heat Transfer Area- 79.96 SF  Tube design gauge pressure- 110 psig  Tube outside diameter-1 in  Shell design gauge pressure- 68.6 psig  Tube seal type- seal welded tube joints  Tube pitch symbol- triangular  Expansion joint- No  Cladding location- shell  # tube passes- 1  # shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vendor grade- high  Regulation type- none |
| Dist-cond acc- horizontal drum | 12700 | 132900 | Design gauge pressure- 15 psig  Design temp- 32 deg F  Operating temp- -395.672712 deg F  Manhole diameter- 18 in  # manholes- 1 |
| Dist- reboiler | 30400 | 101900 | Heat Transfer area- 209.7 SF  Tube design gauge pressure- 110.304 psig Tube design temperature- 377.8 deg F  Tube design operating temperature- 327.8 deg F  Tube outside diameter- 1 in  Shell design gauge pressure- 68.6373 psig  Shell design temp- 332.52 deg F  Shell operating temp- 282.52 deg F  Tube length extended- 20 feet  Tube wall thickness- 0.125 in  Tube pitch- 1.25 in  Tube pitch symbol- triangular  Cladding location- shell  # tube passes- 2  Duty- 1.14 MMBTU/hr  Vaporization- 90%  Specific gravity tower bottoms- 0.5  Mol. Weight bottoms- 100  Heat of vaporization- 150 btu/lb  TEMA type- BKU |
| Dist- reflux pump | 4200 | 26200 | Fluid head – 225 feet  Fluid specific gravity- 1  Driver type- motor  Seal type- single mechanical seal  Design gauge pressure- 15 psig  Design temperature- 32 deg F  Fluid viscosity- 1 Cpoise  Pump efficiency- 70%  Steam gauge pressure 400 psig  Primary seal pipe plan- none  Secondary seal pipe plan- none  Cooling water pipe plan- none  Pipe plan pipe type- welded pipe/fittings |
| Dist- tower |  |  | Tray type- sieve  Application- distil  Vessel diameter- 2 feet  Vessel tangent to tangent height- 82 feet  Design gauge pressure- 15 psig  Design temperature- 332.52 deg F  Operating temperature- 282.52 deg F  Tray material- A285C  # Trays- 35  Tray spacing- 24 in  Cladding materials- none  Fluid volume- 20%  Jacket type- full  Molecular weight product- 73.8  Tray thickness- 0.1875 in  ASME design basis- D1NF (Division 1, no fatigue)  Start Stop cycles \* 1000- 1  Pressure cycles \* 100- 0  Pressure amplitude- 0%  # of hydrostatic tests- 20  Temperature cycles \* 1000- 0  Temperature amplitude- 0% |
| Heat | 31400 | 124600 | Heat Transfer area- 1409.179665 SF  Tube design gauge pressure- 18.637333 psig  Tube design temperature- 650 deg F  Tube operating temp- 550 deg F  Tube outside diameter- 1 in  Shell design gauge pressure- 35.304 psig  Shell design temp- 650 deg F  Shell operating temp- 600 deg F  Tube length extended- 20 feet  Tube wall thickness- 0.125 in  Tube seal type- seal welded tube joints  Tube pitch- 1.25 in  Tube pitch symbol- Triangular  Expansion joint- NO  Cladding location- Shell  # Tube passes- 2  # Shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vandor grade- High  Regulation Type- None |
| Separator | 29000 | 183300 | Liquid Volume- 2132.829606 gal  Vessel diameter- 5.5 feet  Vessel tangent to tangent diameter- 12 feet  Design gauge parameter- 15 psig  Vacuum design gauge parameter- -14.696  Design temp- 600 deg F  Operating temp- 550 deg F  ASME design basis- D1NF (Division 1, no fatigue)  Start Stop cycles \* 1000- 5  Pressure cycles \* 100- 0  Pressure amplitude- 0%  # of hydrostatic tests- 20  Temperature cycles \* 1000- 0  Temperature amplitude- 0% |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |
| Heater | 8000 | 44900 | Heat Transfer area- 6.740545 SF  Tube design gauge pressure- 110.304 psig  Tube design temperature- 377.8 deg F  Tube operating temp- 327.8 deg F  Tube outside diameter- 1 in  Shell design gauge pressure- 68.637333 psig  Shell design temp- 250 deg F  Shell operating temp- 122 deg F  Tube length extended- 20 feet  Tube wall thickness- 0.125 in  Tube seal type- seal welded tube joints  Tube pitch- 1.25 in  Tube pitch symbol- Triangular  Expansion joint- NO  Cladding location- Shell  # Tube passes- 2  # Shell passes- 1  Weld Xray- 20%  TEMA type- BES  Vandor grade- High  Regulation Type- None |
| Mixer |  |  |  |
|  |  |  |  |

The information from the above chart comes from an Aspen Plus simulation which was sent to Aspen Icarus Process economic analyzer to determine sizing and costing of individual pieces of equipment.

E Cost- Equipment Cost

D- Direct Cost

1. Economic Evaluation factored from equipment cost

Propionic acid is used in many daily processes such as plastics and food preservatives and without it or an alternative to Propionic acid the quality of life would decrease. Propionic acid was chosen mostly due to its ability to preserve food and have it last longer. The longer shelf life that food has the more affordable it will become as food vendors will not have to throw away as much food, as their expiration times are increased by preservatives.

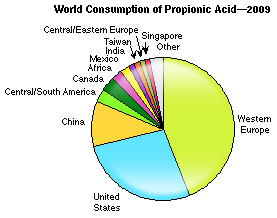


Figure VII.1: World Demand of Propionic Acid

In the above figure it can be seen that the United States is the second largest user of Propionic acid coming in second to Western Europe. As Western Europe is a region it can be inferred that the United States is the nation with the largest usage of Propionic acid. This information is encouraging to team Echo because it can be reasoned that because the U.S. is using so much Propionic acid that there must be a sizable demand for the product.

Figure VII.2: Price of Propionic Acid over the past decade

As can be seen in the above figure the price of Propionic acid has been steadily increasing over the past decade approximately doubling. This reinforces the idea that there is a great demand for Propionic acid. After all, with the increasing price and no decrease in the amount of Propionic acid used it can be inferred that it is very important and necessary. This is most likely due to the wide range of uses of Propionic acid. The relevance of establishing that there is a great demand for Propionic acid in this country is to determine the longevity of the project and whether or not it will pay out. The life of this project should be quite long as the demand for Propionic acid is not decreasing and is projected to rise over the next few years. As team Echo intends to target its sales towards food companies and the demand for food is always around without question, team Echo feels that this project will be profitable and long lasting.

If all 33,000 tons of Propionic acid is sold each year then the process will gross approximately $ 59.4 million per year. The yearly gross price in conjunction with all of the costs that will be incurred are used to establish a breakeven point. The sooner the breakeven point occurs, the sooner that the process will begin to make money.

1. Utilities

Feed-Effluent heat exchangers are used in the process in order to transfer heat to where it needs to be. This option is preferable to solely using steam to heat the process and cooling water to cool. The reason this is true is because by simply moving the process heat some of the utility costs that would have gone into steam and cooling water is eliminated. Cooling water and steam cannot be eliminated entirely because the system because the system is exothermic overall and the heat transfer will not be satisfied without hot and cold utilities.

Cooling water will be used in the process in order to heat exchange the excess heat of the system. An energy balance was done in order to determine how much water was needed to cool both of the reactors to a reasonable temperature and that amount is 9.0 E5 lb/hr cooling water (7.56E5 to cool the first reactor, and 1.45E5 lb/hr for the second reactor).

Steam that has been generated from the excess heat will be used to power a turbine. This turbine will be creating electricity. There is approximately a 30 percent energy loss in the production of electricity. The total energy of the energy sinks is ??? and the excess energy is 8.74E7 btu/hr.

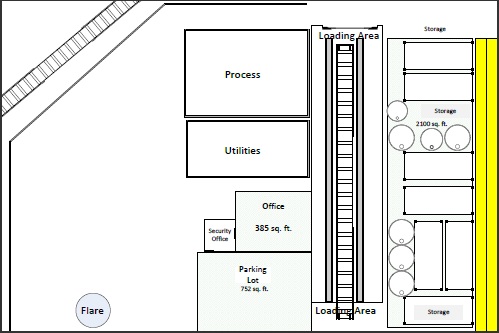
The plant will require around ten workers. Each of these workers will be paid a base pay of $20/hr. Workers will have a maximum of 4 weeks of vacation time which does not roll over, thus if not used it will be lost. Workers will start will 1 week of vacation every year they will be evaluated as to whether or not they are permitted more paid vacation time.

In addition to these 4 weeks of vacation 5 sick days per year will also be given though In order to ensure that the plant is fully staffed at all times there will be four differing shifts that have been arranged so that there should be no overlap, and also so that there will always backup workers in case an absence should occur.

As leadership is always necessary one individual form each shift will be selected in order to become a shift manager. The shift manager will be required to select an approved backup manager. The shift manager and back up will be paid $28/hr and $24/hr respectively. The shift manager and the backup cannot be absent at the same time.

Benefits will include basic health care through United health care. This is strictly medical and there is no copay as the beneficiary and their dependents will have a maximum of $3000/yr to spend on health care per year. An advantage 90 Drug Program comes with this plan which will allow the employees to obtain any prescribed generic drugs for free from all participating Walgreens. Dental insurance will also be supplied through Unicare.

1. Conceptual control Scheme
2. General Arrangement (Plant Layout)



1. Distribution and End- Use Issues review
2. Constraints Review
3. Feedstock Definition

Synthesis gas or syngas is a gaseous mixture primarily comprised of Carbon Monoxide and Hydrogen. The syngas that will be utilized by team Echo will be created from coal obtained from Illinois Coal Basin number 6. Because the syngas is coming from coal, desulfurization will need to take place as Sulfur can be harmful to catalysts. CO2 sequestion will also take place in order to have a greater purity of syngas. Coal is an abundant resource that is currently the second greatest provider of energy, coming in second only to petroleum. This coupled with projections that coal will indeed be around for at least the next two hundred years leaves hope that obtaining the necessary coal for synthesis gas will not be a problem.

Ethylene is the other portion of feedstock utilized in the synthesis of Propionaldehyde. Ethylene is currently being produced and sold at large quantities at Lyondell Basell in Morris, Il. For this reason, as is discussed in Location Sensitivity Analysis, both team Echo and Foxtrot have decided to be located there. As the location of the plant will be extremely close to this particular feedstock, the transportation constraint has been eliminated. As for the production of ethylene, it is an abundant hydrocarbon that is easily synthesized and hopefully will not be an issue in availability.

1. Conversion Technology Description

Both of our reactors will be compressed heat exchanger reactors, obtained from Chart Energy and Chemicals Inc. This specific type of reactor allows for the reaction of gas phase feeds as well as the immediate removal of heat from the system utilizing Brazed Aluminum as the reactor material. Both reactions that take place in this process to synthesize propionic acid (synthesis of propionaldehyde followed by the oxidation of the aldehyde) are highly exothermic and will require a medium to absorb all that heat in efforts to reduce the cost of energy for the plant as a whole. This specific type of reactor allows for the immediate absorption of exothermic heat which can then be used to generate steam or to increase the temperature for streams later in the process. The synthesis of the aldehyde intermediate takes place under the influence of a Rh based catalyst which will be on a solid support, to account for this, Chart Energy and Chemicals creates a specific type of the compressed heat exchanger reactor with room to place packing materials inside the open channels of the reactor.

The standard compressed heat exchanger, without room for packing materials, will be utilized for the oxidation of propionaldehyde as the catalyst for this reaction is a dissolved cobalt salt.

1. Separation Technology Description

There are multiple methods of separation in this process such as distillation columns, flash separators, decanters and precipitation and filtration.

The flash is the separation process used to remove reactants from the outlet stream of the initial reactor. This separator operates at 70ᵒF and 14.7psi and removes most of the reactants from the aldehyde that is synthesized in the reactor.

The next form of separation is the distillation column used after the oxidation reactor. The purpose of this distillation column is to remove anything still in the stream that is not the desired acid, water and cobalt which is dissolved in the water. This column has a distillate rate of .95 lbmol/hr, reflux ratio set at 2, 35 stages and the feed stage above stage 18. The stream of interest is the one exiting the bottom of the column which contains the acid.

This stream then has the cobalt salt precipitated and filtered out from solution to be reused as the catalyst for the oxidation of the propionaldehyde.

After the filtration, some of the water, as well as a small portion of the acid, is decanted out of the solution and the remaining liquid is fed into the second distillation column which has a distillate rate of 14.2 lbmol/hr, no condenser, and 25 stages with the feed stage above stage 1. The distillate is composed of water and the remaining reactants that have been carried through the process and the bottoms is composed of 99.8 wt% propionic acid.

1. Production Description

The end product of this process will be a 99.8 wt% propionic acid, which is higher than the industrial purity level of 99.5 wt%. Propionic acid is a colorless liquid which gives off a pungent odor; chemically it is a three carbon chain carboxylic acid which has a similar density to water at ambient conditions also this compound is miscible in water much like other short chain organic acids.

1. Location Sensitivity Analysis

The plants producing Propionic acid and syngas will be based in Morris, Il 60450. Team foxtrot based themselves in southern Illinois so as to be near Illinois coal basin number 6. As the syngas that team Foxtrot is producing is quite difficult and expensive to transport, in order to lower costs for both teams it has been decided that team Foxtrot and team Echo will be located next to each other. The determinant factor of team Echo’s location is Ethylene. Ethylene like syngas is quite expensive and difficult to transport. The region near southern Il was scoured to find ethylene production plants, and while the search lead heavily towards Texas and Louisiana eventually Lyondell Basell in Morris, Il was found and settled upon. In Morris, both teams have chosen to be located as close to a rail line as possible in order to minimize the coal transportation costs of team Foxtrot as team Foxtrot will currently be approximately 5 hours away from southern Il.

Morris, Il is a small town that is very historical yet not unwilling for progress. Not only is Morris home to Lyondell Basell and soon to be teams Echo and Foxtrot but it is also home to Dresden nuclear power plant which is one of many plants that supplies power to the Chicago land area. Bill Cheshareck is in charge of all building and zoning permits and is who must be contacted in order to determine what needs to be done in order for plants to be built in Morris.

1. ESH Law Compliance

According to the EPA both propionic acid and propionaldehyde have been classified as non carcinogenic. OSHA classified propionic acid as a non air contaminant.

1. Laws of Physics Compliance
2. Turndown Ratio

In order to have enough time to properly ensure that all machinery is in proper working order and to ensure that any problems can be fixed it is integral a proper turn down ratio is selected. Usual turn down ratios are around 30 days, and team echo will be going with a turn down ration of 28 days, thus the operating year will be 337 days. Team foxtrot will be operating at an 18 day turn-down ratio and thus their syngas will be stored during the 10 days in which the echo plant will not be operational.

1. Applicable Standards

Product 🡪 99.5 (% minimum) Purity Propionic Acid with 0.1(% maximum) Water

Industrial Grade

* + Converted to Calcium, Ammonium, or Sodium salt for preserving feed and foodstuffs
  + Solvent for nitrate cellulose

Quality Control:

Propionic Acid is only sold in pure form with a 99.5 wt % purity, determined acidimetrically. The maximum water content is 0.1 wt %; the sulfate, chloride, and heavy metal content is generally <1 ppm. The color index is normally below 5 APHA. Oxidizable substances (ketones, aldehydes, esters) can be determined from the reaction time in the KMnO4 test. Their proportions should be <0.05 wt %. The standard method for quality control is gas chromatography. Detection is carried out with a flame ionization detector (FID). The corresponding requirements are summarized below.

|  |  |  |
| --- | --- | --- |
| Specification | Limits | Analytical Method |
| **Propionic Acid Content, wt%** | **99.5** |  |
| **Water Content, wt%** | **0.1** |  |
| **Aldehydes, wt%** | **0.05** |  |
| **Readily Oxidizable Substances, wt%** | **0.05** |  |
| **Evaporation Residue, wt%** | **0.01** |  |
| **Iron, ppm (mg/kg)** | **1** |  |
| **Other heavy metals, ppm (mg/kg)** | **10** |  |
| **Platinum – cobalt color, APHA** | **10** |  |
| **Density (20oC), g/cm3** | **0.990-0.998** |  |
| **Bp, oC** | **140.7-141.6** |  |

* Shelf Life: 24 months for drums and 12 months for bulk
  + According to BASF, Propionic Acid has an almost unlimited shelf life in unopened, original containers and when properly stored in a protected storage area.
  + DOW States to attain maximum shelf life and preserve its quality, store under a nitrogen atmosphere and/ or use an appropriate desiccant system to prevent moisture contamination.

Water Solubility: 37g/100 ml

Piping Pressures

According to the ANSI/ASME Grade B Piping Pressure and Temperature Ratings:

|  |  |  |  |
| --- | --- | --- | --- |
| Maximum Allowable Pressure *(psig)* | | | |
| Pipe Size *(inches)* Pipe Schedule | Pipe Size *(inches)* Pipe Schedule | Temperature *(oF)* | |
| 100 | 200 |
| 1” | 40 | 2857 | 2857 |
| 80 | 3950 | 3950 |
| 160 | 5757 | 5757 |
| 1.5” | 40 | 2116 | 2116 |
| 80 | 2983 | 2983 |
| 160 | 4331 | 4331 |
| 2” | 40 | 1783 | 1783 |
| 80 | 2575 | 2575 |
| 160 | 4217 | 4217 |
| 3” | 40 | 1693 | 1693 |
| 80 | 2394 | 2394 |
| 160 | 3600 | 3600 |
| 4” | 40 | 1435 | 1435 |
| 80 | 2075 | 2075 |
| 160 | 3376 | 3376 |
| 5” | 40 | 1258 | 1258 |
| 80 | 1857 | 1857 |
| 160 | 3201 | 3201 |
| 6” | 40 | 1143 | 1143 |
| 80 | 1794 | 1794 |
| 160 | 3083 | 3083 |
| 8” | 40 | 1006 | 1006 |
| 80 | 1586 | 1586 |
| 160 | 2976 | 2976 |
| 10” | 40 | 913 | 913 |
| 80 | 1509 | 1509 |
| 160 | 2950 | 2950 |

Recovery systems:

Exit of 1st reactor – unreacted hydrogen and carbon monoxide

Cobalt catalyst exiting the 2nd reactor 🡪 is then precipitated out and filtered and recycled

Ordinary steel is totally unsuitable for the handling of Propionic Acid. Aluminum is only resistant at room temperature and to anhydrous, concentrated Propionic Acid; at higher temperature corrosiveness toward aluminum varies with the concentration of acid. Thus the corrosion maximum for 50 oC lies at 75% acid, whereas there are two maxima at the boiling point, a weaker one at 1% and a strong one at 99.8% acid. Copper and copper alloys are stable toward Propionic Acid up to its boiling point, but only if the solutions are free from air or oxidizing substances. Of the stainless steels, the ferritic chromium steels (13 – 17% Cr) are unsuitable because Propionic Acid tends to cause pitting. Generally, austenitic CrNi steels and CrNiMo steels are used for handling Propionic Acid. However, impurities in Propionic Acid can make the use of titanium or Hastelloy (e.g., Hastelloy C-22) equipment necessary, even below the boiling point. Above the boiling point, up to about 230 oC Hastelloy C-22 has shown excellent resistance even under oxidizing and reducing conditions. Above 230 oC only silver has proved to be a suitable material.

Containers made of aluminum with a purity of 99.5% or alloyed steels are suitable for storing pure Propionic Acid. Aluminum is unstable toward aqueous Propionic Acid. Polyethylene containers can be used for temporary storage of Propionic Acid and as small packing drums. Plastics are not recommended for long-term storage. Glass-reinforced plastics are unsuitable even for short-term storage. HASTELLOY® C-22® alloy - Used to store the corrosive Propionic Acid, even at high enough temperatures.

1. Project Communications

**Wednesday Conference Meeting 03/30/11**

* Working on plant layout (using google 3-D)
  + google sketchUp
  + can use plot plan 2-D...no need for 3-D
  + also using Visio
* Working on finishing up economics
* PFD is in Visio format
  + post screenshot to make it seen for all

**Tuesday Conference Meeting 03/15/11**

* What is important for process to operate properly
* Need schematic of necessary controls in place
* ISA symbology
* Distillation column- temp, composition, temp change, over head receiver, not dry pump, must have some level in the bottom of the columns, platform wert twenty or thirty feet, platform with ladder
* Hx- must be able to pull tubes, need space for this, orient hot dog style,
* control room, locker room, storage tanks, all equipment must be located, must have access space between equipment

**Notes taken during Meeting 3**

Engineering challenges Use block flow in presentation In Econ, total cost total profit, not all components Spec on period of investment Cost of money that every group will use Interest cost of money Every group will be using the same assumptions Removing gas, there is am adsorption and stripping process Hotel used engineering world for costs or sizing? Must remember to number slides Paired groups do economics together Look into what to do with waste, thermal oxidizer? Adiabatic flash to size heater

**Wednesday 03/09/11 Telecom Meeting**

1. Presented more info than expected, good!
2. Next week, March 14-18, 2011: need to meet with Shannon possibly Tuesday but she’ll email us

So that we can work on:

* + 1. Finalizing PFD
    2. Finalizing Material balance
    3. Preparing proper layout of process
    4. And sizing

1. Need to know flash conditions
2. The new reactor conditions for 1st and 2nd reactors need to be defined
   1. If there’s a temperature rise, state
   2. Address how to get heat out of there
3. Crystallization: it’s a point below saturation
4. there was water in 2nd reaction but need to state
5. search more on cobalt iodide
   1. price
   2. solubility in water, propionaldehyde and propionic acid

**Tuesday 03/08/11 Questions and suggestions made by Mentors:**

Presentation questions:

* sizing of the distillation column are usually ~85 ft for a 35 theoretical stages
* Aldehyde: vapor & flashed
* HX between reactor & flash?
* Streams 4 & 7 should be same temperature
* Bubbling gas through tank, spark O2 to it
* Separation of propionic acid from water, how soluable is it in water?
* Are we crystallizing or precipitation it out of the process?
* Put water on Co catalyst…it will need water make-up stream

**Wednesday 02/23/11 Telecom Meeting**

* We need more details especially on economics in order to increase grade on presentation
* We have more info on nickel carbonyl and it shows up in ASPEN as a gas phase only which is causing a problem because literature says it’s been in liquid form
* Method of recovering our catalyst (cobalt halide)? We’re getting high reflux ratio
* Ask Prof. Nitche on ASPEN
* CSTR deals with liquids but our design is not a CSTR, can use for place holder, think about using PFR…
* Use dielstein…orgo synthesis
* Look at patents for using catalysts
* Post correction on Wiki of specs
* What manufacturers use our catalyst?
* If it’s only one stream we’ll have to keep buying new, if we know price and what we need, we can get by with this
* Use ASPEN for equipment sizing but not all of them
* We need details on one of the operations in terms of sizing, looking at one area and making sure we have everything we need, look at it more closely and make sure everything is checked
* Energy sinks, look at where energy is coming from and into deltaH across a reactor
* We will have to see the design and sizing of reactor which ASPEN does not recognize

**Thursday 02/17/11 Telecom Meeting**

* Write abstract by Monday 02/21 as it is due then
* 5-6 page progress summary is due on midterm day, week 8
* Email CoX manufacturers to get conversion rates and other important information
* Integrate catalyst into Aspen
* Look into catalyst interaction and recovery
* MSDS sheets for more safety information
* Fix economics, no more place holders
* Use knovel in research
* Divide utilities cost with Foxtrot
* Reactor information, CSTR implies liquid
* Pumps compress liquids and Compressors compress gasses
* Find out about Drew’s catalyst
* Prove that separation is occurring in all separators
* Heat of compression
* Reciprocating compressors don’t go above 250 °F use multistage

**Tuesday 02/15/11 Questions and suggestions made by Mentors:**

* Note the sources of the info and numbers brought up
* Note the $/yr or day or month that are being calculated in the pricing and economics
* Use scientific notation, commas, an overall number to describe an estimate without many and ongoing significant figures
* Price of syngas is high...get a better estimate
* Estimated capital cost is very low, get a better estimate
* There are equipment/steps needed in the process such as: decanter, recycle, to recover catalyst on regular basis
* something to make sure catalyst doesn't go anywhere wrong
* heat removal step
* where to flash out product
* CSTR is a design reactor or are we modeling it like that in aspen?
* show what it is/what it's like
* How do we get aldehyde out of liquid?
* stick with outline as placed in beginning of presentation
* include capital cost in a safety system
* place process overview with total #s in and out, this can be displayed in a diagram
* improvise the block flow diagram to show what's in the streams and display numbers

**Meeting with our mentor**

* Do we need refrigerant at recycle stream? When reaction is happening at high temperature. Show her price of refrigerant and if ok to use.
  + Depending on where we are letting out to…not necessary
* How much refrigerant/cooling water we need?
  + How much heat is generated should tell us how much cooling water we need
* How much catalyst we need? How to find that?
* How long for 1st and 2nd…may not need large volume. How long we need to be in, residence time. Ask Dennis/Bill
* Find reactivity and selectivity
  + Do we need cooling tower?
  + Sharing with other grp their cooling tower.
  + Look into air coolers
  + Look into heat effluent exchange
* Cobalt propionate or cobalt halide which to choose?
* How to include catalyst in aspen?
* Have you contacted Adam Kenya about the Sulfur concentration of syngas from foxtrot?
  + She talked to him but Adam will talk to foxtrot so that they find a solution for it.
* Specifics on utility costs? What do we include?
  + Add into the ppt
* Use multiple stage compressors with ethylene
* More hydrocarbons are stored in spheres
* Vapor pressure will be high for ethylene

Things to add to the power point:

* Add a row for temps and pressures for each stream number
* Enthalpy can be found from aspen in the stream summary, use those, they’re fine. If we don’t want to use, address that we don’t and state how we’ll find it.
* Change 30kt/yr to English units
* Fix environmental review=add nickel carbonyl
* Nickel Carbonyl: OSHA has permissible exposure: 0.001ppm for gen industry, threshold limit is 0.05ppm, grp1 human carcinogen.
* Cobalt Iodide: OSHA 0.1 cob/m3 (rate 3-reacts explosively with water)
* Fix block flow diagram update according to aspen-kevin
* Update competing process slide (we are doing 1st rxn but we’re not doing 2nd)
* Fix graphs, sharpen view
* Cheaper to transport coal than ethylene-slide “plant location” fix it
* Interest on loans we’re getting to build…we have negative cash flow initially?
* How long will it take to build the plant?
* Delete 3rd point on slide: estimates
* Slide: catalyst of nickel carbonyl change unit to English
* Plant Standards EPA, ASME (for pipe standards), OSHA, and FDA: find out product purities, to be generally recognized as a safe list,
* Price graph: need a current date
* MB in hand calc
* Catalyst life? Nickel bought every yr but cobalt, include the cost as an initial cost as well as annual
* Selectivity of catalyst?
* Recovery of catalyst? Flash, not sure if we’re getting 100%
* We r reacting in gas phase in 1st reactor

**Thursday, February 10, 2011, Conference call**

* what we are working on:
* Material and Energy Balances
* Aspen flowsheet
* Aspen Material Balance
* Hand calculations
* Economics
* pricing on catalysts
* Cobalt (II) Iodide
* Nickel Carbonyl
* Utility costs
* Plant Economics
* List of things to look over again:
* Flow sheet with flag streams
* MB & EB around multiple pieces of equipment in a table
* State how this process is going to close
* Need units from lb/yr to lb/hr
* Pay attention to significant figures
* State the hrs/yr the plant will run
* Number all streams on flow sheet
* Look further into:
* What is the syngas coming out at (T & P)?
* Run Economic Analysis
* Size compressors with knowing what's coming in
* Multiple stages for compressor

**Thursday February 3, 2011, Conference call**

* What we are working on:
  + economic evaluation
  + carbon or stainless steel?
  + over 800 F cant use carbon
  + material and energy balance
  + have an in-progress aspen flowsheet for material balances
  + will start on energy balances soon
* Location: Morris, Il
  + make sure its close to a railroad so its easy for foxtrot to transport coal.
  + Send flowsheet to Shannon when done
* Next conference call: Thursday, February 10th at 1:00 pm
* Discuss time for in person meeting with Shannon
* On the table:
  + Get to Shannon's work after senior design
  + Friday evenings after 4

**Friday January 28, 2011**

Joint Team Meeting: Foxtrot and Echo.

Shannon Brown, Adam Kanyuh

* Purpose of the meeting:
  + Things seem in "flux"
  + Establish a feed basis (should be given to team Foxtrot by Monday)
* What we need to do:
  + Send an email to Foxtrot, Shannon and Adam stating the composition and the feed rate required
  + what contaminants can we ignore?
  + what will poison our catalyst?
  + what exactly are our requirements?
  + Location?? (information needs to be handed over to Foxtrot sometime next week.)
  + ﻿its easier to transfer coal compared to transferring ethylene, so this decision should be made as a joint group.
  + some locations to look into:
  + st. louis (marathon petrochemical plants)
  + do they sell ethylene crackers?
  + gulf coast
  + look up where ethylene crackers are readily available
  + send a few locations to foxtrot so they have a choice as well
  + Utility conditions?
  + Are there any conditions that both the teams need?
  + compare conditions with foxtrot and determine if there is anything we both can use
  + example: steam pressure levels
* What we know:
  + Echo needs syngas to be at these ranges:
  + temp: 250-300 C
  + pressure: 100-300 bar
  + Echo is using nickel carbonyl and cobalt as catalysts
  + Foxtrot currently want their gassifier to be located in Illinois # 6 Basin/Butiminous
  + located in southern illinois

**Notes from first meeting with Shannon (Jan 23, 2011) meeting:**

* Spec of impurities to gasifier team
* How pure is the feed stock?
* What would poison the catalyst
* Produce 80 kilotonne/year? Share of world market?
* Outline of what we are covering – week by week
* On powerpoint
* Look at schedule
* Focus of the week
* Economic analysis of buying vs. making ethylene
* Add quantity to design basis
* Check up solid support for catalyst
* Autoclave? Does it dissolve better?
* Acyl rhodium tetra carbonyl
* Lowers temp to 45 C
* Ceramic catalyst- talk to Meyers
* State of catalyst?
* Rough economics – meeting two
* Set up report on wiki
* More on environment review after catalyst

**Meeting: January 20, 2011**

Working Title: Synthesis of Plastics from Propionic Acid

Design Basis: Why we need to produce plastic. (In Discussion)

Plastics being looked at:

* Polyethylene
  + Polyethylene (or polyethene, polythene, PE) is a [family](http://www.ehow.com/relationships-and-family/) of materials categorized according to their density and molecular structure. For example, ultra-high molecular weight polyethylene (UHMWPE) is tough and resistant to chemicals, and it is used to manufacture moving machine parts, bearings, gears, artificial joints and some bulletproof vests. High-density polyethylene (HDPE) is used to make milk jugs, margarine tubs and water pipes. Medium-density polyethylene (MDPE) is used for packaging film, sacks and gas pipes and fittings. Low-density polyethylene (LDPE) is soft and flexible and is used in the manufacture of squeeze bottles, sacks and sheets.
  + Read more: [Uses of Thermoplastics | eHow.com](http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBHf3eN) <http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBHf3eN>
* Teflon
  + Teflon is the brand name given by DuPont Corp. for a polymer called polytetrafluoroethylene (PTFE), which belongs to a class of thermoplastics known as fluoropolymers. It is famous as a coating for non-stick cookware. Being chemically inert, it is used in making containers and pipes that come in contact with reactive chemicals. It is also used as a lubricant to reduce wear from friction between sliding parts, such as gears, bearings and bushings.
* Read more: [Uses of Thermoplastics | eHow.com](http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBarTNg) <http://www.ehow.com/about_5436147_uses-thermoplastics.html#ixzz1BcBarTNg>
* *Leaning towards making propionic acid -> polyethylene*

**Wednesday January 19, 2011 (first meeting as a group)**

* Do some research by second group meeting
* Advantages and Disadvantages of gasses being looked into:
* Propionic acid:
  + Naturally occurring
  + Made from ethylene and carbon monoxide
  + Uses and advantages:
  + Analgesic
  + Intermediate product for thermoplastic
* Formic acid:
  + May cause damage to optic nerves
  + Made from methanol, ammonia sulfuric acid, and carbon monoxide
  + Also made from water and carbon monoxide
  + Cheapest to make?
  + Operating at a high partial pressure
  + Simplest carboxylic acid
* Acetic acid:
  + Global demand: 6.5million tonnes/year
  + Made from carbon monoxide and methanol

1. Competing Processes

Industrially, Propionic Acid is currently produced almost exclusively by three different processes:

1) Carbonylation of ethylene with carbon monoxide and water

2) Oxidation of Propanal

3) Direct oxidation of hydrocarbons

The Koch synthesis has been investigated intensively. As a carbonylation reaction of ethylene in a strongly acidic medium, it is a variant of the Reppe synthesis. However, compared with the latter it never achieved much industrial significance and was carried out with little success.

Other possible sources of Propionic Acid, which are not used industrially for economic reasons, are its formation as a byproduct in the high- and low-pressure carbonylation of methanol to give acetic acid (2% formation of Propionic Acid), the direct reaction of ethylene, carbon monoxide, and water over noble-metal catalysts.

Two-step reactions have been described, in which Propionic Acid is obtained directly from synthesis gas (20 – 60 bar, 150 – 160 oC, Rh catalysts). With the current availability of ethylene and naphtha these processes are, however, not yet competitive. It is sometimes desirable, to use Propionic Acid produced by natural methods, particularly for the use of Propionic Acid in flavors and fragrances. Appropriate microbiological and enzymatic processes have been developed, which are usually based on the anaerobic fermentation of starch or sugars. However, the expensive production of this “natural” Propionic Acid limits its use to special areas of application.

**Carbonylation of Ethylene (BASF Process) (Our Old Process)**

In the Reppe synthesis ethylene is reacted with carbon monoxide and water in the presence of Ni(CO)4 (Nickel Carbonyl) according to the following process: the reaction takes place at high pressure and is characterized by low raw material costs, high conversion, high yield, and a simple workup. Ethylene and carbon monoxide are compressed and continuously pumped into the high-pressure reactor together with the feed solution. The crude Propionic Acid formed at 100 – 300 bar and 250 – 320 oC is drawn off at the head of the reactor and cooled in a heat exchanger with production of steam. Part of the cooled reaction product is recycled to the reactor for temperature regulation, the majority of it is allowed to expand and is separated into an off-gas and a crude acid stream. Nickel is recovered from the offgas and led back into the reactor. The off-gas is incinerated with recovery of heat. The crude acid stream is subsequently dehydrated and worked up by distillation in several following columns. The nickel salts that are formed are recycled into the process. The pure Propionic Acid is finally obtained by distillation. The product residue is channeled out of the process. Variants of the Reppe and Koch syntheses are possible, where the effect of inorganic salts on the reaction conditions and yield are important factors. Boric acid is reported to accelerate the reaction and hinder the precipitation of catalyst salts.

**Oxidation of Propanal (Our Process)**

The oxidation of propanal is an important route to Propionic Acid. This route is economically attractive although two steps (production of propanal and subsequent oxidation) are required: (1) Propanal is formed in large quantities as an intermediate in the production of npropanol by hydroformylation of ethylene, and (2) the oxidation takes place in plants in which other aliphatic carboxylic acids (n-butyric and isobutyric acids, n-valeric and isovaleric acids) are also produced. A high utilization of available capacity is therefore guaranteed in both steps.

**Propanal Production**

The production of propanal is carried out by the hydroformylation of ethylene. It is favored because, unlike the case of the higher aldehydes, n/isomixtures cannot be formed. Two syntheses compete: the classical cobalt- catalyzed high-pressure carbonylation at 200 – 280 bar, and 130 – 150 oC, and the rhodium- or iridium- catalyzed low-pressure carbonylation at about 20 bar, and about 100 oC. In the high-pressure synthesis the yield is generally impaired by partial hydrogenation of propanal to give propanol. The isolation of the aldehyde takes place, after removal of cobalt, by distillation of an azeotrope with ca. 98% aldehyde content. In the low-pressure synthesis (Union Carbide), the aldehyde can be distilled directly from the reaction mixture in 99% purity.

**Oxidation**

Propanal is subsequently oxidized under very mild conditions at 40 – 50 oC to Propionic Acid with high selectivity. In the United States Propionic Acid is produced by the oxidation of propanal by Union Carbide and Eastman Kodak.

**Direct Oxidation of Hydrocarbons**

A large quantity of Propionic Acid is obtained by the direct oxidation of hydrocarbons, predominantly naphtha. In this process, which is principally used for acetic acid production, formic acid, Propionic Acid, and an isomeric mixture of butyric acids are formed as byproducts. Whether this process is considered economic for Propionic Acid production is principally a question of the market evaluation of the different products. The process has favorable raw material costs, but requires a relatively complex workup of the product mixture. The composition of the acid mixture formed in the oxidation can be affected by the reaction conditions (pressure, temperature), the type of reactor (tubular reactor, column reactor), the raw material (naphtha, liquefied petroleum gas), and by the catalyst. If naphtha is used, the proportion of Propionic Acid in the mixture is about 10 – 15%. In other cases like with 2- methylpentane as a raw material, the proportion of Propionic Acid can increase to 31%. The total yield of acids does, however, vary considerably with the starting material. **BP Chemicals Process**

Naphtha is preheated to 170 oC and oxidized with air at 40 – 45 bar in several reactors in series. Again, the heat of reaction is used for steam generation. The cooled discharge from the reactors is separated from the reaction off-gas in a separator. Entrained liquid is recovered from the off-gas and recycled to the reactor; the off-gas is then incinerated. The liquid reactor discharge is separated into an organic phase, which contains unreacted hydrocarbons, and an aqueous phase which contains the product mixture. The unreacted hydrocarbons are recycled to the reactor. The low- and high-boilers are separated from the aqueous phase which then gives the crude acid. From this the C1- to C4-acids are obtained by extractive dehydration followed by fractional distillation. Propionic Acid is produced by direct oxidation at BP Chemicals (UK), Hoechst – Celanese (United States), and Daicel (Japan).

1. Information Sources and References

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